

## **An Overview of Capillary Electrophoresis In Element Speciation Analysis of the Environment**

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## Abstract

This article focuses on the main developments in element speciation analysis by capillary electrophoresis (CE) since the 1990s. A brief description of the main techniques employed in CE analysis has been reviewed with emphasis in the chemical species derived from inorganic forms and organic compounds bound to metal and non-metal elements. Analysis of the most important elemental species existing in the environment and biological fluids has been discussed employing the many different separation techniques available in CE analysis. Special attention has been paid to simple analytical methods but multiple element analysis of chemical species has also been considered. The great advances of modern CE equipments coupled to atomic absorption, inductively plasma emission and mass spectrometry as detection systems make possible to compete with HPLC for this purpose. Analysis of arsenic, chromium, iron, mercury, lead and tin species in their inorganic and organic forms has been discussed in more detail for their relevance in environmental chemistry.

## 1. Introduction

IUPAC defined speciation as the distribution of an element amongst defined chemical species in a system (1). However, from an analytical point of view, the speciation of an element can also be described as determination of the individual physicochemical forms of that element that together make up the total concentration in a sample (2).

Elemental species after being released into the environment are of paramount importance because of both beneficial and harmful effects depending on the concentration and chemical form of the metal species. The importance of element speciation analysis has lately been emphasized in literature (3). In order to highlight the relevance of this type of analysis it must be said that chemical and biochemical forms of the elemental species present in the environment determine the extension to which these species can be available to biota.

Metals in water exist in an equilibrium state under multiple forms. Metals can be physically separated into two fractions: soluble and insoluble (suspended matter). The scope of this paper refers to the distribution of the chemical species in the soluble fraction.

From Simkiss and Taylor (4), the following forms of the elements are considered

- a) free metal ions under different oxidation states, e.g. Fe(II) and Fe (III) cationic species
- b) oxoanions, e.g. As(III) and As (V) anionic species
- c) charged and uncharged inorganic complexes, e.g. chloro mercury and chloro mercuric complexes
- d) organometallic complexes, e.g. methyl tin

in order to simplify the discussion of this work.

Since usually an environmental sample contains more than one elemental species and because of the presence of interferences which can make difficult and complex the analysis a separation step in the process is necessary. Among the different separation techniques, gas chromatography (GC) and liquid chromatography (HPLC) can be mentioned as powerful and efficient ways to achieve this purpose (5,6). However, capillary electrophoresis (CE) has been used in recent years as an alternative to the traditional methods for speciation analysis because of its interesting features including high separation efficiency, short analysis time, low sample consumption and low operating cost. Since separation in CE is mainly governed by difference in charge to size ratio of analytes, this technique is extremely useful in chemical speciation studies (7,8).

The successful approach for speciation analysis depends on two factors: selectivity and sensitivity which means the ability to discriminate all the metal species involved in the study and to determine the amounts of each species at the levels present in the sample to be analyzed.

Different detection methods have been applied in CE for identification and quantitation of metal species in environmental analysis: UV light, mass spectrometry (MS) in its different modes (electrospray, collision-induced dissociation), inductively coupled plasma (ICP). They have been employed as unique detectors or coupled in tandem like MS and ICP interfaced to CE. Fundamentals and the practical aspects of interfacing CE with ICP-MS were reviewed (9).

CE separations can be accomplished through different modes of operation including capillary zone electrophoresis (CZE), micellar electrokinetic chromatography (MEKC), capillary isoelectric focusing (CIEF), capillary electrochromatography (CEC), as well as newly developed microchip capillary electrophoresis (MCE). A brief of these techniques has been discussed by Liu et al. (8).

## 2- Element Speciation Analysis of the environment

### 2.1 Metals, metalloids and organometals

Metals and metalloids are present in all compartments of our environment and the environmental pathways of these elements are of high importance in relation to their toxicity towards all forms of life.

Their concentration levels, mobility, transformation and accumulation processes in the ecosystem depend on parameters such as pH, redox conditions, temperature, presence of organic matter and oxygen, and finally the action of microorganisms. All these factors strongly influence the biogeochemical cycles of elements in the environment.

From an environmental point of view, there is an important group of substances that consist of metals combined with organic groups. They are organometallic compounds which share many properties with organic compounds in general. These organic groups attached to metals are mainly produced by environmental processes. Except in few cases, ecotoxicological studies have evidenced that organometallic compounds are much more toxic than the ions of the corresponding inorganic compounds. The toxicity varies in relation to the compound, e.g. trialkyl tin species are more toxic than mono- and dialkyl tin compounds. At the same time, the impact on biota depends on the organism investigated.

### 2.2 Types of Element Speciation Analysis

Speciation analysis can be performed in at least five different types, depending on the aim and scope of the analytical investigation (10). A summary of the main characteristics of each of these analysis is given as follows:

#### 2.2.1 General physical and chemical speciation

Speciation is carried out in 3 compartments: air, water and soil. It is directed to investigate chemical and biochemical processes. Physicochemical studies are mainly addressed to analyze the various fractions taken from samples of each compartment.

### 2.2.2 Screening speciation

Analysis is directed to the detection and determination of one definite analyte. Examples are alkyl Sn and alkyl Hg in water, sediment, organisms, etc.

### 2.2.3 Group speciation

Speciation analysis leads to the determination of the concentration level of a specific group of compounds or a specific element in different compounds or the same element in a particular oxidation state. An example is the determination of levels of concentration of mercury (elemental, inorganic and organic forms).

### 2.2.4 Distribution speciation

Speciation studies are related in most cases to analyze biological samples. An example is the determination of heavy metals in plants.

### 2.2.5 Individual speciation

Analysis is a difficult task and it is carried out by separation techniques like chromatography or electrophoresis coupled to multiple detection systems. An example is identification of unknown chemical species as to molecules, complexes, electronic or nuclear structures.

## 3. CE in speciation analysis of the elements

This section reviews the background of CE in element speciation analysis of the environment. A brief of the modes and detection techniques reported in literature is described.

### 3.1 Iron

To our knowledge, Aguilar et al. (11) could separate the Fe (II) and Fe (III)-cyanide complexes in their work considered the first report on method speciation by CE. The complexes were separated in only 5 min using on-column UV detection at 214 nm. Detection limits were lower than 10  $\mu$ M and the method was improved by Buchberger and Haddad (12). The speciation of Fe in most reported studies involved complexation of the two oxidation states species prior to electrophoresis (13,14,15,16,17). Podzniakova et al. (18) could selectively separate the two species in an on-line procedure using 1,10-phenantroline and 1,2-cyclohexanediaminetetraacetic acid. Detection limits were 0.06 mg/L for Fe (II) and 0.1 mg/L for Fe (III). Speciation of Fe in environmental samples like water-soluble iron in atmospheric aerosol was carried out using the two complexing agents mentioned above.

It should be pointed out that oxidation of Fe (II) by air is one of the major difficulties in Fe speciation. Air must be excluded or oxidation prevented during sample preparation. Closed beaker digestion proved to be appropriate in a work developed by Ashdown and Marriott (19). They could obtain the best recoveries in two certified reference materials.

### 3.2 Chromium

The most common oxidation states of chromium found in chemistry are 0, III and VI. The interest in determining the concentration of the specific chemical form of chromium, rather than only its total concentration, is the fact that the chemical form can have a pronounced effect on its mobility, bioavailability and toxicity. In biological systems, the anionic hexavalent chromium is extremely mobile, dangerous and toxic.

Several CE methods have recently been reported for the separation of Cr (III) and Cr (VI). As much as both species are oppositely charged, they show different electrophoretic mobility and it has not been an easy task to achieve the simultaneous determination of the two species by a CE method.

The first work about CZE separation of Cr species with a conventional UV detector has been reported by Semenova et al. (20). By a conversion of Cr (III) in an anionic species by complexation with EDTA before the electrophoresis of the sample containing the chromate ion they achieved the simultaneous determination of the two species. The detection limits were 50 ng/ml for Cr (III) and 10 ng/ml for Cr (VI). Later on, several authors (21,22) also reported the simultaneous determination of Cr (III) and Cr (VI) in the CZE mode with UV detection. However, the detection limits of these works do not accomplish the levels required for the analysis of real samples.

Chan and Chan (23) could achieve detection limits of 10 ppb of Cr by coupling CZE to ICP-AES. Also, CE-ICP-MS methods have been tried with success by Olesik et al. (24) and Kinzer et al. (25). Detection limits of 10 ppb for both species in less than 10 min were achieved without the use of complexing agents or additional steps for their simultaneous determination.

From an environmental point of view electroplating and other industries require a precise control of their effluents and it is important to reduce the levels of toxic species of chromium. CE methods afford an important tool for the control of Cr (VI) and safety in effluents discharged from electroplating and dyestuff industries.

### 3.3 Arsenic

Reports on speciation of As involve the most numerous papers respect to the analysis of the rest of the elements. The reason for research on As speciation is based on its effects on human health and the environment and it is also associated with the toxicity of its compounds.

The nine species containing As in their molecules must commonly determined are the following compounds: arsenite (As (III)), arsenate (As (V)), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), phenylarsenic oxide (PAO), phenylarsenic acid (PPA), p-amoniphenylarsenic acid (p-ASA), 4-nitrophenylarsenic acid (4-NPAA), 4-hydroxy-3-nitrobenzenearsonic acid (ROXARSONE). In general, inorganic As is most toxic than arseno organic compounds. The latest As compounds are used as animal feed additives and their residues are discharged to the

environment. Sun et al. (26) using counter- and co- EOF mode could achieve the separation and quantitation of the nine As species by direct UV spectrophotometric detection.

Even when conductivity detection has been used in As speciation by CZE with slight higher sensitivity improvement with respect to the photometric mode, several authors published the separation and quantitation of inorganic and organic As species by the two detection systems (27,28). Not only As but also Se, Sb and Tl have been speciated by Casiot et al. (28) using indirect UV detection at 254 nm. Sodium trimethyltetradecylammonium hydroxide (TTAOH) was employed in order to reverse the direction of electroosmotic flow and to increase the migration velocity of the compounds studied. Lin et al. (29) first reported the advantages of using CE-ICP-MS for the determination of As (III), As (V), MMA and DMA. Detection limits of 1-2 µg/L in drinking and soil leachate were achieved by Holderkebe et al. (30).

### 3.4 Selenium

Selenium is an important element that possess important features and properties. Today, Se is specially studied for its industrial, environmental, biological and toxicological significance. In environmental and biological samples, Se exists in both inorganic and organic forms. Inorganic Se (IV), Se (VI) anionic forms and different organic compounds in which Se is bound to C like aminoacids, proteins and sugars are some examples of the distribution of this element in various chemical and biochemical species in a wide range of molecular masses and charges. Various separation and detection methods combined with preconcentration techniques are presently used for the separation of Se species.

Regarding Se determination, several approaches have been cited in literature (31). CE with UV detection for the quantification of Se (IV) and Se (VI), selenomethionine and selenocysteine has been reported by Albert et al. (32). A modifier like TTAB was added to the buffer in order to reverse the electroosmotic flow. Separation was obtained with detection limits in the order of mg/L units. When chromate was added as background electrolyte to the buffer and indirect UV detection was employed the sensitivity was increased in the range from µg/L to tens of µg/L for the inorganic Se species. Higher efficiencies in CE separations have been achieved by Li and Li (33) applying the field amplification sample injection (FASI) technique to enhance sensitivity (33,34,35) 12 µg/L of Se (IV) could be detected as the limit (10) but even lower values were reached.

ICP-MS interfaced to CE exhibits interesting advantages in element speciation analysis. This technique allowed to improve the detection (36), specially in samples containing organic and bioinorganic selenium compounds (37).

Identification and detection of 4 organic Se species in fractions of human milk have been reported in several works of Michalke et al. (38). After size-exclusion chromatography the milk fractions collected were analyzed by CE coupled to ICP-MS system and their approach was applied in the identification and recovery of Se species. Different strategies were tried in order to overcome identification problems caused by shifts of migration times caused by differences in ionic composition of the treated samples and the standard solutions (39).

### 3.5 Tin

In the environment, it is more important to determine tin organic compounds than inorganic tin for the abundance and variety of the organic forms of Sn formed in the aquatic media and living organisms. Today, more than 800 organotin compounds are known and most of them are of anthropogenic origin except methyltin which can also be produced by biomethylation.

CE coupled with various detection modes was employed for determination of tin species (40,41,42,43). Since most of organotins possess poor chromatographic properties, indirect UV is a common detection mode (43,44). Determinations of trimethyl Sn, triethyl Sn, tributyl Sn (TBT) and triphenyl Sn (TPhT) were reported by Pobozy et al. (44). 2 µg /ml of TBT and 0.2 µg/ml of TPhT were the values of detection limits achieved by these authors. Also, cyclodextrine (CD) employed as modifier in the electrolyte in the separation of a mixture of di- and tri- organotins was reported by Whang and Whang (43). Detection limits were in the range between 1.2 and 1.7 µM. Fluorescence detection has also been tried with enhancement of sensitivity at a level of 1 mg/L of Sn as limit of detection. However, the concentration sensitivity is still not sufficient for the routine control of the environment in which a level of µg /L as detection limit is generally required. Some methyltins have been analyzed by CE coupled to atomic spectroscopy instruments but these techniques have not extensively been applied in environmental samples (45).

### 3.6 Lead and mercury

Inorganic and organic lead species have been reported by different authors (46, 47). Special interest is governed by the toxicity and wide distribution of triethyl lead and dimethyl lead in the environment as final products of industries and transport circulation.

Li and Li (48) applied a MEKC method using a preconcentration method by extraction and evaporation in heavily polluted samples with success. However, they could not determine these compounds in tap water taken from a car park. Lately, Liu and Lee (49) could determine different inorganic and organic species derived from mercury, lead and selenium by CE using EDTA as complexing agent. FASI technique was employed and detection was carried out by UV absorbance. In this way, sensitivity was enhanced more than 1000 fold the levels of the charged species reaching detection limits under 1 ng/ml (48) Proton-Induced X-ray (PIXE) detection was also tried by Vogt et al. (50) for the determination of lead species increasing the sensitivity of CE method in speciation analysis.

In the case of mercury, CE was applied in the determination of inorganic and organic forms of Hg in the environment. Mercury exists as Hg (0), Hg (I) and Hg (II) species and in a wide variety of chemical forms that have different biological and environmental behavior (51). Methylation of inorganic Hg is one of the most important transformations as a result of the conversion of inorganic forms in methyl, dimethyl and trimethyl mercury forms, specially caused by natural biotic processes. Toxicity of the later species is much higher than inorganic Hg.

A CE method for the separation of organomercurials has been developed by Medina and co-workers (52). In a quite simple method, mercury at a level under 1 mg/L in biological materials of marine origin, was determined. The cation  $\text{CH}_3\text{Hg}^+$  in the samples was extracted with 0.1% cysteine solution prior to CE analysis. Afterwards, the technique was improved by Carro-Diaz et al. (53). Sample stacking (54) was also tried reaching to lower the detection limits under 12 ng/g of organic Hg in the extracted tissue. If dithizone sulfonate is used instead of cysteine to separate and detect various Hg species it was possible to achieve better sensitivity (2 ng of methylmercury per gram) (54, 55).

The best results were obtained when ICP-MS was coupled to CE in samples extracted as cysteine complexes at alkaline pH. Values at few ppb levels of Hg could be obtained in environmental samples using this technique (56, 57, 58). When ICP-MS detection was coupled to CE after separation of volatile species in sodium borohydride solution (58), values of 1-30  $\mu\text{g/L}$  of Hg could be attained. Accuracy of the method examined by analysis of reference materials gave good results.

### 3.7 Other elements

In the environment some other elements exist in various organic and inorganic forms like vanadium and antimony have also been reported in literature (59, 60).. Different CE procedures employed in separation of these element species was achieved by interfacing various detection systems.

Antimony presents severe difficulties due to lack of stability of Sb compounds. However, Sb (III) and Sb (V) have been determined by Casiot et al. (28) using a CE method with indirect UV detection. The values of detection limits were 64  $\mu\text{g/L}$  for Sb (III) and 147  $\mu\text{g/L}$  for Sb (V) respectively. Organoantimony compounds like trimethyl Sb could be first determined by CE and published by Michalke and Schramel (48) at levels in the range of 0.1 and 0.7  $\mu\text{g/L}$  as the lowest values of detection.

### 4 Present and future trends

Hyphenated techniques mostly CE-ICP-MS can resolve analysis of elemental species at moderately abundant concentrations, and possibly in the next years those species existing at trace levels will also be evaluated. Commercial interface systems have widely been developed at a much higher degree in the last time and they will compete with conventional HPLC equipments mostly employed in this field. Multi-elemental applications of ICP-MS as detectors of CE equipments is an attractive aspect to consider in development of new analytical methodologies taking into account that it is possible not only to diminish LOD values but also to achieve higher resolution capacity respect to the rest of detectors usually employed in this task (61, 62, 63, 64)..Optical detectors continue to be employed in CE analysis of inorganic ions and in the way to be extended to other forms of the elements. However, electrochemical detection specially contactless conductivity detectors (CCD) show multiple applications and probably they will grow more than conventional systems.

Miniaturization and portable CE devices are some of the recent advances in instrumental technology with applications both in laboratory control analysis and in on-campus studies of the environment. An interesting review on element speciation accounting for recent progresses in analytical CE instrumentation has been published by Timerbaev (65).

### 5. Conclusions

Undoubtedly, element speciation analysis is one of the most difficult tasks of analytical chemistry.

CE is a promising technique to solve this task with great advantages such as simplicity, less expensiveness, high resolution, sufficient flexibility and the possibility to act as a separation system feasible for interfacing with multiple and different types of detectors. Day by day, CE is gaining wide attention due to its multiple and favorable features over other techniques like GC and HPLC. However, despite CE is considered a non disturbing technique of the original sample composition some troublesome aspects of the analysis must be overcome. The influence of electrophoretic buffer composition must be emphasized in order to obtain reliable and meaningful results. Another feature to attend is the selection of the experimental conditions during the electrophoretic run because of the same reason mentioned above. Detection of elements by ICP-MS has widespread employment in the field of analysis of element species. Successful applications of this particular detection system coupled to CE have been produced in the last years owing to the advances of new analytical methodologies. Finally, the availability of certified reference materials of environmental interest together with inter and intra laboratory tests must be underlined in order to assure the stability and reliability of the results obtained both in standards and samples..

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